THERMODYNAMIC ANALYSIS AND PHASE EQUILIBRIA CALCULATION OF Ga-In-Sb SYSTEM

by

IMON MUKERJEE

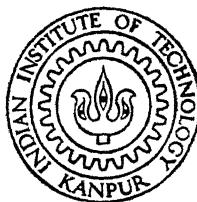**DEPARTMENT OF METALLURGICAL ENGINEERING**

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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in Partial Fulfilment of the Requirements
for the Degree of

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by

IMON MUKERJEE

to the

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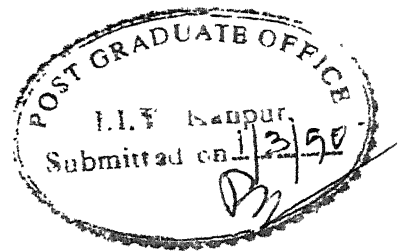
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CERTIFICATE

It is certified that the present work entitled "THERMODYNAMIC ANALYSIS AND PHASE EQUILIBRIA CALCULATION OF GA-IN-SB SYSTEM " has been carried out by Mr.Imon Mukerjee under my supervision and that it has not been submitted elsewhere for a degree.

FEBRUARY 1990

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Imon Mukerjee

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ABSTRACT

The binary Ga-In and the ternary Ga-In-Sb phase diagrams are calculated in this study. A quasi-sub-sub regular model is used to describe the thermodynamic properties of the liquid phase in the Ga-In and Ga-In-Sb systems. The solid phase in the Ga-In system is represented by Wagner's dilute solution model. The solid phase in the Ga-In-Sb system is represented by a regular solution model. Marquardt's Bsolve algorithm is used to optimize the values of model parameters. The fit to thermodynamic and phase diagram data using the optimized model parameters is found satisfactory.

CHAPTER 1

INTRODUCTION:

In 1963, Gunn discovered a property exhibited by certain semiconductor materials known as the 'transferred electron effect'. This effect is instrumental in the generation of microwave oscillations in bulk semiconducting materials. The effect was found by Gunn to be exhibited by gallium arsenide and indium phosphide, but cadmium telluride and indium arsenide have also subsequently been found to posses it. These materials have got a very peculiar band structure, which results in the following effect: with the application of a voltage within a critical range, they exhibit a 'negative resistance' characteristic. Negative resistance means, decrease in current with increase in voltage, a property reverse to that seen in normal ohmic conductors. Such materials are called Gunn Diodes. When a Gunn Diode is tuned with a L-C circuit and a critical D.C. voltage is applied, it generates an oscillating impulse in the microwave range. Gunn diodes are used extensively in radars, aircraft's rate-of-climb indicator, burglars alarm and in all types of microwave receivers and instruments (1).

Till the end of 1960's, Gallium arsenide was supposed to be the optimum material for Gunn diodes. But in the 1970's, new materials, exhibiting better transferred electron properties were seen. One of them was $Ga_xIn_{1-x}Sb$

$(0.8 \leq x \leq 0.95)$. In 1974, Sakai et al (2) showed that $Ga_xIn_{1-x}Sb$ was the best Gunn Diode material, particularly at x=0.5. Kawashima et al (3) proposed that $Ga_xIn_{1-x}Sb$ materials for use in Gunn diodes can be suitably prepared from epitaxial materials made by Liquid Phase Epitaxy on InSb or GaSb substrate.

Epitaxy is the process of growing single crystal semiconductor layer on a single crystal semiconductor substrate with perfect lattice matching. Liquid Phase Epitaxy is the growth of epitaxial layers by direct precipitation from liquid phase. It is the most suitable for growing thin layers ($\geq$ 0.2 μm), as it has a slow growth rate.

To control the composition of the epitaxial layers, knowledge of phase diagrams of the constituent systems is essential.

A large number of experimentally obtained thermodynamic and phase diagram data are available on the Ga-In-Sb system. In this study, phase diagrams are theoretically calculated by fitting various thermodynamic models to the available experimental data.

Why calculate Phase Diagrams ?

The reasons are as follows:

1. To develop mutually consistent mathematical description of the phase equilibria and thermodynamic properties of a system.

2.   The methods of phase equilibria calculations may be used to reduce the number of experiments that are needed to experimentally determine a phase diagram, particularly useful for ternary and higher order systems where large number of experiments are normally needed to determine a phase diagram.

3.   Extrapolation of the phase diagrams into regions where no experimental data is available or experiment is difficult to perform.

4.   The phase equilibria calculation activity may help in the digital computer storage and retrieval of the phase diagram and thermodynamic information.(4).

CHAPTER 2

LITERATURE REVIEW

2.1   The Ga-Sb and In-Sb systems :

The binary Ga-Sb and In-Sb systems have been recently reviewed and calculated by Sharma et al (5). The thermodynamic model and values of parameters obtained by them are used in this study.

2.2   The Ga-In system :

The earliest work reported on this system was by Boisbaudran (6) in 1885. Due to the high cost and scarcity of the metals, his study was limited to only four alloys. He obtained a concave liquidus curve. French et al (7) were the first workers to study the Gallium Indium binary system extensively in 1936-37. They studied a series of some forty alloys of Ga-In covering the entire composition range, starting from pure Gallium to pure Indium. They also obtained a concave liquidus curve, with a eutectic at $16^{\circ}C$ and 16 at% In, and the maximum solid solubility of Ga in In to be 14.8 at% Ga (= 85.2 at% In) at the eutectic temperature. In 1952, Svirbely and Selis (8) reinvestigated the Ga-In system. From electrical resistance versus temperature measurements of several alloys over the entire concentration range, the Ga-In phase diagram was obtained. They reported a concave liquidus curve in the In-rich side of the phase diagram, which gradually changed to convex from an inflection

point at around 70 at% In.   The eutectic point reported was
16.7 at% In and 15.7°C. Their liquidus curve shows large
discrepancy when compared to that of French et.al(7)[Fig 1].
Bros et al (9) measured the heat of mixing of Ga-In alloys at
156, 268, 469°C using a very sensitive Tian-Calvet
calorimeter. Their results show that heat of mixing, ΔH, is
independent of temperature in the range 150-469°C and can be
represented as

$$\Delta H = 4435.0 \quad X_{Ga} \cdot X_{In} \qquad \text{(J/gm-atom)},$$

where X_{Ga} and X_{In} are the atom fractions of Ga and In
respectively. Heubner and Wincierz (10) determined the
solubility of Ga in In and found it to be relatively small.
The maximum solubility of Ga in solid In was found to be 3.3
at% Ga at 15.9°C.   They also measured a number of liquidus
temperatures by thermal analysis. Macur et al (11) measured
the activities of both the components in the Ga-In system
using multiple Knudsen-cell effusion technique.   Their
results show positive deviations from ideality for activities
of both the components. Predel and Stein (12) determined the
enthalpies of mixing of liquid alloys in the   Ga-In system
using a high-temperature calorimeter. The maximum value for
ΔH was found to be 1205 J/gm-atom at 50 at%.   The phase
diagram was evaluated from the measured enthalpies of mixing,
the entropies of mixing and the thermodynamic activities.
Hayes and Kubaschewski (13) reassessed the Ga-In system in
1969 and calculated the Ga-In liquidus lines from
thermodynamic data published till then. The reported
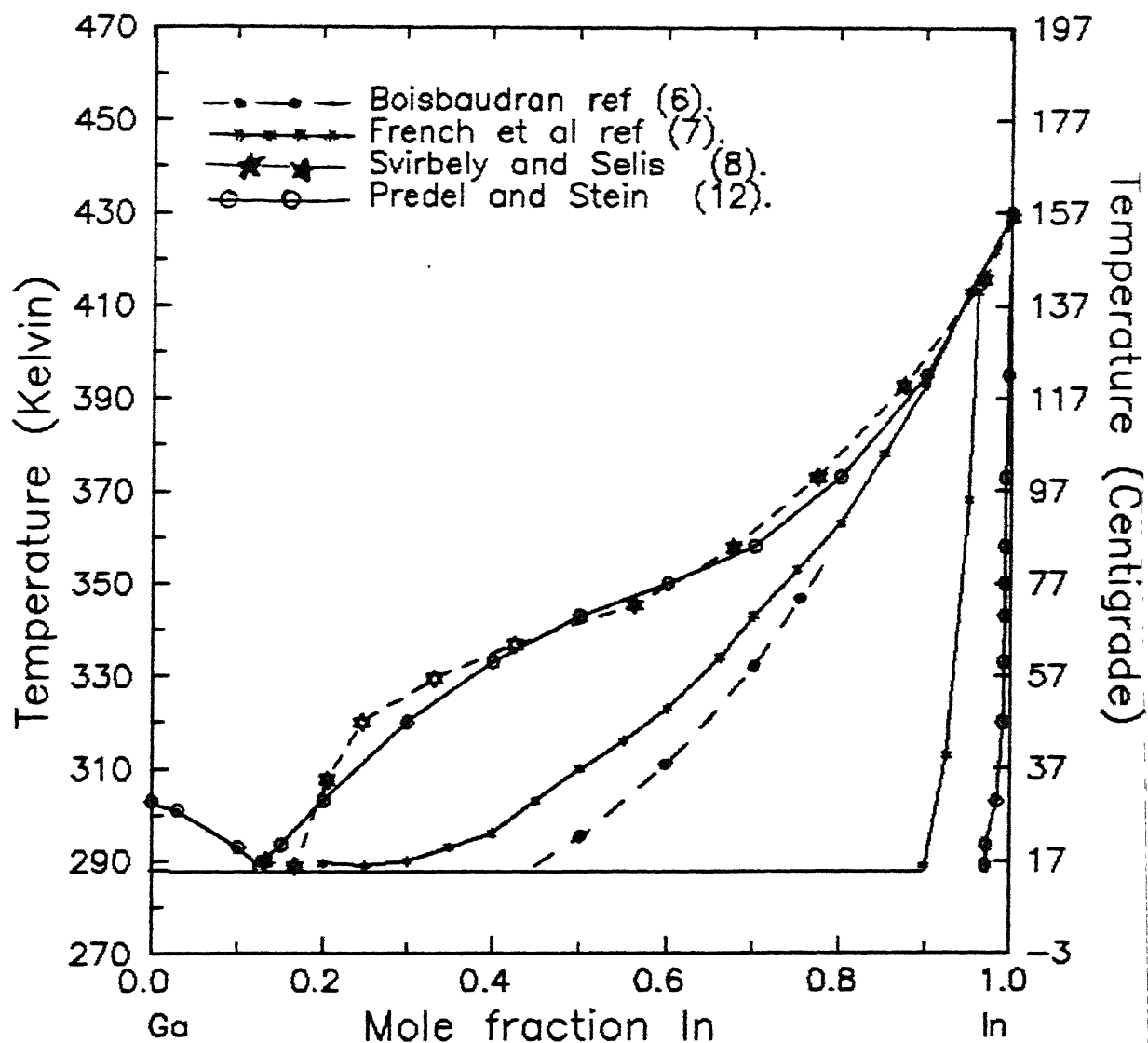eutectic point was 15.8°C and 14.2 at% In.   Rao and Tiller

Fig 1:Comparison of experimental phase
diagram data of Ga—In system.

(14) computed the Ga-In phase diagram using linear programming optimization technique. The calculated eutectic temperature was 16.0°C and the maximum solubility of Ga in In at the eutectic temperature as 16.0 at% Ga.

According to the theory developed by Hume-Rothary, the range of solid solution of one metal in another is determined largely by the relative atomic (or ionic) radii of the constituent metal atoms. If the difference of atomic radius is more than 15 %, the probability of solid solution formation is low. Taking the atomic radius of Ga and In to be 1.41 and 1.66 Å respectively, we find that the percentage difference in their atomic radius is 17.7. So, due to an unfavorable size factor only border-line solubility of Ga in In is expected and vice versa. Examining the available data we find that Heubner et. al (10) reports the maximum solubility of Ga in In as 3.3 at% Ga, which seems to be more realistic than other authors (7,8,13) whose reported values are on the higher side. Solubility of In in Ga is found to be negligible by all authors (6-14).

Examining the available literature carefully we find that the experimentally obtained phase diagrams of Boisboudran (6), French et al (7), Svirbely and Selis (8), and the phase diagram obtained from the experimental data of Bros et al(9) and Macur et al (11) are all quite different from each other [Fig 1]. Rao and Tiller (14) are the only people to calculate the Ga-In phase diagram, but only for the

In rich side. Also the calculation of the Ga-In phase diagram is necessary if we want to calculate the Ga-In-Sb ternary phase diagram at low temperatures. Due to the above reasons it was thought necessary to calculate the Ga-In system.

2.3   The Pseudobinary GaSb-InSb system.

The stoichiometric compounds GaSb and InSb forming in the two binary systems Ga-Sb and In-Sb at 50 at% Sb   are found to have complete solubility in each other in both liquid and solid phases. A vertical section of the ternary Ga-In-Sb phase diagram at 50 at% Sb gives a pseudobinary phase diagram between the compounds GaSb and InSb.

The GaSb-InSb system attracted a lot of attention during the 1950's due to their potential use in the semiconductor industry. Initial works on this system are reported by Köster and Thoma (15) in 1955.   They found GaSb-InSb to form a degenerate eutectic diagram without appreciable terminal solid solution.   But the contemporary work by Goryunova ,and Fedorava (16) show that the two compounds GaSb and InSb, when mixed together and annealed for a considerable length of time at high temperature completely dissolves in each other, thus contradicting the works of Köster and Thoma(15). Wooley and Smith (17) investigated the GaSb-InSb system in 1958. Due to very slow diffusion rates of the materials and low working temperatures equilibriation was

not reached. So, they used compressed powdered samples for their analysis. From heating curve measurements and X-ray analysis pseudobinary phase diagram was obtained. They report a continuous range of solid solubility, starting from pure GaSb to pure InSb. One year later Wooley and Lees (18) reinvestigated the system, and their results were in full agreement to their previous work. Foster and Woods (19) made thermodynamic analysis of the pseudobinary GaSb-InSb phase diagram based on a model which expresses excess Gibb's free energy of mixing as

$$\Delta G_i^{xs,mix} = B_i . X_1 . X_2 ,$$

where i = solid or liquid and

B_i = parameter of the form A+B.T

X_1 and X_2 are mole fractions of GaSb and InSb respectively. Their calculated values were in good agreement with the experimental data of Wooley and Lees (18). The $Ga_x In_{1-x} Sb$ liquid was reported as perfectly ideal whereas the solid phases showed substantial nonideality. Gerdes and Predel (20) determined the enthalpies of mixing of liquid GaSb-InSb alloys form liquid GaSb and InSb with the aid of a high temperature calorimeter. They reported the maximum value of enthalpy of mixing at 1022 K as 162 J.mole^{-1}.

2.4   The Ga-In-Sb system.

A series of papers (21,22,23,24,25 and 26) have demonstrated the feasibility of calculating phase diagrams in III-V ternary systems based upon the regular or quasi

chemical equilibrium model for the liquid and solid phases. All these calculations depend on the existence of some phase diagram data from which the adjustable parameters, called interaction parameters, can be determined by fitting the calculated phase diagram to the experimental data.

Stringfellow (27), in 1971, developed a method of calculating phase diagrams from information of the temperatures and entropies of fusion of the pure III-V compounds and the electronegativities, energies of sublimation and molar volumes of the three constituent elements. The thermodynamic conditions, for the solid-liquid equilibrium in ternary III-V system may be written as :

$$\ln(X_{AC} \cdot \gamma_{AC}) = \ln\left[\frac{4 \cdot \gamma_A \, \gamma_C \, X_A \, X_C}{\gamma_A^{sl} \, \gamma_C^{sl}}\right] - \Delta S_{AC}^f (T_{AC}^f - T)/R.T.$$

$$\ln[(1 - X_{BC}) \cdot \gamma_{BC}] = \ln\left[\frac{4 \cdot \gamma_B \, \gamma_C \, X_B \, X_C}{\gamma_B^{sl} \, \gamma_C^{sl}}\right] - \Delta S_{BC}^f (T_{BC}^f - T)/R.T$$

where X_{AC} and X_{BC} are mole fractions γ_{AC}, γ_{BC} are the interaction parameters, ΔS_{AC}^f and ΔS_{BC}^f are the entropies of fusion and T_{AC}^f and T_{BC}^f are the melting points of the compounds. X_A, X_B and X_C are mole fractions and γ_A, γ_B, γ_C are interaction parameters of the elements, the superscript 'sl' indicating stoichiometric liquid. Activity coefficients in the liquid solutions can be calculated using the regular solution model. They calculated the pseudobinary and found a good fit to the liquidus but deviation was

observed from solidus data at the GaSb rich side. Blom and
Plaskett (28) determined the ternary phase diagram for
Ga-In-Sb experimentally and theoretically. The experimental
procedure essentially consisted of submerging a weighed bar
of GaSb in a melt of Ga:In:Sb of known composition till
equilibrium was reached, then measuring the weight loss of
the GaSb bar to get the liquidus composition. They used a
model similar to the one used by Stringfellow (27) for the
calculation of the phase diagram. The theoretical curve
were found to fit the experimental data satisfactorily.
Antypas (29) determined the liquidus and solidus points at
500° C by experiment similar to that by Blom and Plaskett
(28) mentioned earlier. Solidus points were found by liquid
phase epitaxy measurements. Their experimental values did
not match well with that calculated by Bolm and Plaskett
(28). Since similar discrepancies have been reported for
other III-III-V alloys (viz. Ga-Al-As,In-Ga-P and Ga-Al-P),
they conclude that regular solution models used earlier by
Stringfellow (27) and Blom and Plaskett (28) are inadequate
for describing the III-V systems. Ansara et al (30) measured
the molar excess enthalpies of mixing of liquid Ga-In-Sb
alloys using a high temperature microcalorimeter at 995 K.
They also calculated the ternary phase diagram using a
regular solution model and found the agreement between a few
published experimental data and the calculated points to be
satisfactory. Miki et. al (31) determined the solidus
isotherm at 400° C and the liquidus isotherms at 400, 500,
and 600°C experimentally. They calculated the Ga-In-Sb phase

diagram on the basis of various thermodynamic models, as well as a new model developed by them termed as the modified Delta Lattice Parameter (MDLP) model. The M D L P model was found to fit better than the DLP and regular solution models used so far. Gratton and Woolley (32) experimentally determined the solidus isotherms and isoconcentration lines in the Ga-In-Sb ternary system by means of a technique of annealing samples in the two-phase liquid-solid field and quenching. They compared the results with the data predicted by the simple solution model. It was shown that while the model can give values of the liquidus isotherms in good agreement with the available experimental data, the predicted solidus isotherms and isoconcentration lines are very different from the experimental data. No reasonable variation of the interaction parameters in the simple solution model they used can eliminate this discrepancy and it was seen that in the case of this particular ternary system the simple solution model was of no value for prediction of solidus data.

From a critical study of the literature it was found that, although several models like quasi-chemical, DLP etc and their subsequent modifications are used to calculate the Ga-In-Sb phase diagram, they do not give simultaneous best fits to pseudobinary and ternary data and other thermodynamic properties like enthalpy, entropy etc. The modified DLP model is best among all these, but it is too complex for easy mathematical manipulation.

Sharma et al (5) have found that the quasi-sub-sub regular model fits the Ga-Sb and In-Sb systems very well. Consequently, this model, which has so far not been tried to ternary III-V systems is used in this study to represent the behavior of the liquid Ga-In-Sb phase. The advantage that can be derived out of this model is: any thermodynamic quantity can be expressed as simple functions of mole fraction and temperature .

Thermodynamic Models and Phase Equilibria:

3.1   MODELS FOR LIQUID PHASE :

3.1.1   The binary Ga-Sb and In-Sb and Ga-In systems:

The liquid phases in the Ga-Sb and In-Sb binary systems are represented by the quasi-sub-sub regular solution model. In this model, the integral excess Gibb's energy of mixing is (33):

$$\Delta^l G^{xs} = R.T. \left[w^l_{ij} . x_j + w^l_{ji} . x^l_i - 4.0 . v^l_{ij} . x^l_i \ x^l_j \right] x^l_i . x^l_j \qquad [1]$$

$$\text{where} \quad w_{ij} = A_1(i,j)/T + A_2(i,j) + A_3(i,j) \ \ln \ T. \qquad [2a]$$

$$w_{ji} = B_1(i,j)/T + B_2(i,j) + B_3(i,j).\ln \ T. \qquad [2b]$$

$$v_{ij} = C_1(i,j)/T + C_2(i,j). \qquad [2c]$$

x_i and x_j are mole fractions, $A_1(i,j)...C_2(i,j)$ are constants, i and j = 1, 2 or 3, where 1, 2 and 3 corresponds to Ga, Sb and In respectively in this study. The superscript 'l' is used to indicate the liquid phase.

Applying the well known relation

$$\overline{G}_i = G_m + (1 - x_i) . \left(\frac{\partial \ G_i}{\partial \ x_i} \right)_{K_j} \qquad [3]$$

where the subscript K_j indicates that the ratios between the other components are kept constant, the partial Gibbs energy of mixing of the different components are expressed as

$$\Delta^l \overline{G}_i^{xs} = R.T.\ln \gamma_i = R.T.x_j^2 \left[2.w_{ji}. x_i + w_{ij}(1 - 2.x_i) \right.$$
$$\left. - 4.v_{ij}x_i \ (2 - 3 \ x_i) \right] \qquad [4]$$

The liquid phase in the Ga-In system is represented by a regular solution model. The quasi-sub-sub regular

solution model given in equation [1], under the condition that $v_{ij} = 0$ and $w_{ij} = w_{ji}$, degenerates to the regular solution model.

$$\Delta^L G^{xs} = R.T.w^L_{ij}.x^L_i.x^L_j. \qquad [5]$$

3.1.2   The ternary Ga-In-Sb system:

A quasi-sub-sub regular solution model, with an added parameter (w_{123}) to take care of any ternary interactions , is used to represent the liquid phase in the Ga-In-Sb system (33),i.e.,

$$\Delta^L G^{xs} = R.T.\frac{1}{2}.\sum_{i=0}^{3}\sum_{j=0}^{3}\left[\left\{w^L_{ij} + (w^L_{ij} + w^L_{ji}).x^L_j - 4.0.v^L_{ij}.x^L_i.x^L_j\right\}.x^L_i.x^L_j\right.$$
$$\left. + w_{123}\, x_1\, x_2\, x_3 \right]. \qquad [6]$$

$w_{123} = M + N/T$ M and N are constants.

Applying relation [3] to equation [6], an expression for partial molar Gibb's energy of mixing is obtained.

$$\Delta^L \bar{G}^{xs}_p = R.T. \ln \gamma^L_p = R.T\left[\sum_{i=0}^{3}\left\{(w^L_{ip} + w^L_{pi})/2\right.\right.$$
$$+ (w^L_{ip} - w^L_{pi}).(x^L_p - x^L_i/2) - 8.v^L_{ip}.x^L_i.x^L_p\right\}.x_i .$$
$$-\sum_{i=0}^{3}\sum_{j=0}^{3}\left\{w^L_{ij}/2 + (w^L_{ij} - w^L_{ji}).x^L_j - 6.v^L_{ij}.x^L_i.x^L_j\right\}.x^L_i.x^L_j .$$
$$-w_{123}.(2.x_1.x_2.x_3 - x_1.x_2.x_3/x_p)\right] \qquad [7]$$

where $\Delta^L \bar{G}^{xs}_p$ is the partial molar excess Gibb's energy and γ^L_p is the activity of component p in the ternary liquid.

$$\frac{b(1)}{T} + b(2)$$
$$b(I)\, R. \quad + \quad b(2)\, (RT).$$

3.2   MODELS FOR SOLID PHASES:

3.2.1   Ga-Sb and In-Sb systems :

In the Ga-Sb and In-Sb phase diagrams solid solubility of GaSb in Sb or Ga and InSb in In or Sb or vice versa are negligible.

3.2.2   Ga-In system:

The solid solubility of In in Ga is negligible.

As solid solubility of Ga in In is found by Heubner et al (10) to be 3.3 at% Ga, the solution of Ga in In is considered as a dilute solution and its thermodynamic properties expressed in terms of Wagner's [34] interaction parameter. Accordingly, the activity coefficient of Ga in In is expressed as

$$\ln \gamma_{Ga}^{s} = \ln \gamma^{\circ} + \epsilon \cdot X_{Ga}^{s} \qquad [8]$$

where γ° is the activity coefficient at infinite dilution and ϵ is the Wagner's 1st order interaction parameter. ϵ expressed as a function of temperature can be written as

$$\epsilon = B_{1} + B_{2}/T, \quad \text{where } B_{1} \text{ and } B_{2} \text{ are constants.}$$

Taking reference state of Ga to be an infinite dilution in In, we get the partial molar free energy of mixing for Ga to be

$$\overline{G}_{Ga}^{s} = {}^{\circ}G_{Ga}^{*} + R.T.\left[\epsilon_{Ga} \cdot X_{Ga}^{s} + \ln X_{Ga}^{s} \right] \qquad [9]$$

where ${}^{\circ}G_{Ga}^{*}$ is the free energy of Ga with respect to the new standard state. So, equation [8] reduces to
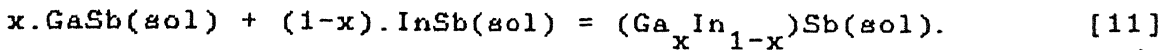
$$\ln \gamma_{Ga}^{s} = \epsilon \cdot x_{Ga}^{s} \qquad [10]$$

Gibbs-Duhem integration on equation [10] gives :

$$\gamma_{In}^{s} = -\frac{1}{2} \epsilon \, x_{Ga}^{s^{2}} .$$

3.2.3   GaSb-InSb   phase :

Let us consider the following reaction to occur forming the solid compound (Ga_xIn_{1-x}) Sb from the constituent solid compounds GaSb and InSb.

$$x.GaSb(sol) + (1-x).InSb(sol) = (Ga_xIn_{1-x})Sb(sol). \qquad [11]$$

The Gibbs energy of formation of solid $(Ga_xIn_{1-x})Sb$ from pure solids GaSb and InSb can be written as :

$$G^m = x.{^\circ G}_{GaSb} + (1-x).{^\circ G}_{InSb} + .R.T.\left[x.\ln x + (1-x) \ln (1-x)\right]$$
$$+ R.T. \ x.(1-x).A^s. \qquad [12]$$

.where $A^s = A_1 + A_2 / T$, A_1 and A_2 are constants.

Partial molar Gibb's energies of the compounds GaSb and InSb are then given by :

$$\overline{G}_{GaSb} = {^\circ G}^a_{GaSb} + R.T.\ln x + R.T (1-x)^2.A^s. \qquad [13]$$
$$\overline{G}_{InSb} = {^\circ G}^a_{InSb} + R.T.\ln (1-x) + R.T \ x^2.A^s. \qquad [14]$$

3.3   PHASE EQUILIBRIA:

3.3.1   Ga-In-system:

For In rich side : $\overline{G}_{In}^s = \overline{G}_{In}^l$ $\qquad [15].$

$\overline{G}_{Ga}^s = \overline{G}_{Ga}^l$ $\qquad [16].$

Expanding equation [15]:

$${^\circ G}_{In}^s + R.T.\left[\ln x_{In}^s + \ln \gamma_{In}^s \right] = {^\circ G}_{In}^l + R.T.\left[\ln x_{In}^l + \ln \gamma_{In}^l \right].$$

$$i.e., R.T.\left[\ln \frac{x_{In}^l}{x_{In}^s} + \ln \gamma_{In}^l - \ln \gamma_{In}^s \right]$$

$$= {^\circ G}_{In}^s - {^\circ G}_{In}^l = \Delta^\circ G_{In} \qquad [17].$$

Similarly, form equation [16]., we get

$$R.T. \left[\ln \frac{x_{Ga}^{l}}{x_{Ga}^{s}} + \ln \gamma_{Ga}^{l} - \ln \gamma_{Ga}^{s} \right]$$

$$= {}^{o}G_{Ga}^{*} - {}^{o}G_{Ga}^{l} = \Delta^{o}G_{Ga}^{*} \qquad [18]$$

Here $\Delta^{o}G_{In}$ is the standard Gibb's energy of formation of solid In from liquid, and $\Delta^{o}G_{Ga}^{*}$ is the standard Gibb's energy of formation of Ga from liquid phase, reference state taken as infinitely dilute solid solution of Ga in In. From the calculations of Sharma et al (5), we have

$$\Delta^{o}G_{In} = -3263.52 + 7.5934.T \qquad J/mole. \qquad [19]$$

The value of $\Delta^{o}G_{Ga}^{*}$ can be expressed as

$$\Delta^{o}G_{Ga}^{*} = C_{1} + C_{2}.T \quad , \text{ where } C_{1} \text{ and } C_{2} \text{ are constants.}$$

Similarly, for the Ga rich region, since the solubility of In in Ga is negligible, we can write:

$$\overline{G}_{Ga}^{s} = \overline{G}_{Ga}^{l} . \qquad [20]$$

i.e., $R.T. \left[\ln \gamma + \ln x \right] = {}^{o}G_{Ga}^{s} - {}^{o}G_{Ga}^{l} = \Delta^{o}G_{Ga} \qquad [21]$

where, $\Delta^{o}G_{Ga}$ is the standard Gibb's energy of formation of solid Ga from liquid phase, x and γ are the mole fractions and activity coefficients respectively. From Sharma et al (5), we have

$$\Delta^{o}G_{Ga} = -5589.82 + 18.453 T \qquad [22]$$

The equations 17 ,18 and 21 are simultaneously optimized using the MARQUARDT'S BSOLVE algorithm.

For optimization of parameters, liquidus data of Predel et al (12) were used. The solidus points were

obtained from the graph of Predel et al (12). The values of the experimental point of Heubner et al(10), giving the maximum solubility of Ga in In was also used.

3.3.2 Ga-In-Sb system :

For equilibrium between liquid Ga-In-Sb and solid compound $(Ga_x In_{1-x})$ Sb is given by

$$\bar{G}^l_{Ga} + \bar{G}^l_{Sb} = \bar{G}^s_{GaSb} \qquad [23a]$$

$$\bar{G}^l_{In} + \bar{G}^l_{Sb} = \bar{G}^s_{InSb}. \qquad [23b]$$

Expanding equation [23a],

$$\Delta^\circ G^{l \rightarrow s}_{GaSb} = {}^\circ G^s_{GaSb} - {}^\circ G^l_{Ga} - {}^\circ G^l_{Sb}$$

$$= R.T. \left[\ln \gamma^l_{Ga} + \ln \gamma^l_{Sb} + \ln X^l_{Ga} + \ln X^l_{Sb} \right.$$

$$\left. + w_{123} X^l_{Ga} \left(X^l_{In} + X^l_{Sb} - 4 X^l_{In} X^l_{Sb} \right) \right]$$

$$- R.T. \left[\ln \frac{X^s_{In}}{0.5} - A^s \frac{(X^s_{Ga})^2}{0.25} \right] \qquad [24]$$

In the above expressions the superscript s represents solid phase, and l liquid phase.

Similarly, from equation [23b] :

$$\Delta^\circ G^{l \rightarrow s}_{InSb} = {}^\circ G^s_{InSb} - {}^\circ G^l_{In} - {}^\circ G^l_{Sb}$$

$$= R.T. \left[\ln \gamma^l_{In} + \ln \gamma^l_{Sb} + \ln X^l_{In} + \ln X^l_{Sb} \right.$$

$$\left. + w_{123} X^l_{In} \left(X^l_{Ga} + X^l_{Sb} - 4 X^l_{Ga} X^l_{Sb} \right) \right]$$

$$- R.T. \left[\ln \frac{X^s_{Ga}}{0.5} - A^s \frac{(X^s_{In})^2}{0.25} \right] \qquad [25]$$

In equations [24] and [25] the expressions of all the activity coefficients are known in terms of mole fraction and temperatures (equation [7]). The values of w^l_{ij}, w^l_{ji}, v^l_{ij}, ${}^\circ G^s_{GaSb}$, ${}^\circ G^s_{InSb}$, ${}^\circ G^l_{Ga}$, ${}^\circ G^l_{Sb}$ and ${}^\circ G^l_{In}$ are taken from

Sharma et.al (5)(table 2). The unknown parameters are A^s and w_{123}. We now proceed to optimize for the unknown parameters by MARQUARDT'S BSOLVE algorithm.

For the optimization of parameters A^s and w_{123}, liquidus and solidus phase diagram data of Gratton and Wooley(32), enthalpy of mixing data of Ansara et al (30), and pseudobinary phase diagram data of Wooley and Smith (17) were used.

Gratton and Wooley (32) determined the solidus isotherms and isoconcentration lines by means of a technology of annealing the samples in liquid-solid field and quenching. To test the validity of their results, they equilibriated a few samples for 20 days, but no change from the condition observed after 24 hours of annealing was seen. Also the X-ray photographs of powdered samples showed sharp lines and resolved K_α doublet, thus establishing the fact that the samples were homogeneous.

Wooley and Smith (17) experimentally determined the pseudobinary phase diagram by annealing powdered specimens for eight to twelve weeks at temperature near the solidus to get an equilibrium composition. Their data were later supported by experiments done by Wooley and Lees (18).

Because of the above reasons, the data of Gratton and Wooley (32) and Wooley and Smith (17) were taken to be reliable and used for phase diagram calculation.

3.3.3   Pseudobinary GaSb-InSb system:

Pseudobinary phase diagram can be obtained as a special case of the ternary. Fixing the mole fractions of Sb as 0.5 in the solid and liquid phase in the ternary equilibrium equations and solving, we arrive at the pseudobinary GaSb-InSb phase diagram.

Results and Discussions:

4.1   Ga-In system :

The   optimized   parameters $\in$ and $\Delta\ G_{Ga}^{*}$ can be expressed as   :

$$\in\ =\ -74700.0/T\ -\ 2601.06 \qquad\qquad [26]$$

$$\Delta\ G_{Ga}^{*}\ =\ -20030.0\ +\ 49.8132.T \qquad\qquad [27]$$

The values of some critical thermodynamic properties calculated by us are compared to both experimental and calculated values from existing papers (Table 1).

It was found that excess entropy of mixing of Ga in In is independent of of temperature and can be expressed by an equation:

$$\Delta\ S^{xs,m}\ =\ -1.09.\ X_{Ga}\ X_{In} \qquad (J/mole) \qquad [28]$$

$\Delta\ S^{xs,m}$ expressions were also calculated from the data of Hayes and Kubaschewski (13) and obtained from graph of excess enthalpy versus mole fraction given by Predel and Stein (12). A similar expression was found to hold   true. They report values of the constant to be -0.46, and -1.30 respectively.   Ansara et al (30)   reports   a   similar experimentally calculated $\Delta S^{xs,m}$ expression, the value of the constant being 1.14. Examining the above data, it is seen that the calculated value of the constant in this study matches very well with experimental data.   It appears that the value reported by Ansara et al (30) has   a printing

error, the negative sign for the constant has got omitted.

The Ga-In phase diagram is given in Fig 2. The agreement between the experimental and calculated data, is, in general good. French et al (7), Svirbely and Selis(8) and Rao and Tiller (14) reports more than 14 at% solubility of Ga in In, whereas Heubner and Wincierz(10) reports 3.3 at% solubility. Since the atomic radii of Ga and In vary by more than 15 %, according to Hume-Rothary rule, a border line solid solubility of Ga in In is expected. Thus, our result is in good agreement to the Hume-Rothary theory and also matches satisfactorily with that of Heubner and Wincierz (10).

4.2   <u>Ga-In-Sb system</u>

Optimized values of w_{123} and $A^{\text{ß}}$ can be represented as :

$$w_{123} = -399.739/ T - 2.78281 \qquad [29]$$

$$A^{\text{ß}} = 550.771/ T + 0.58052. \qquad [30]$$

Fig 3 shows a comparison between values calculated by us and experimental values of Ansara et al(30) Except for $X_{Ga}/ X_{Sb} = 1/1$, the agreement is satisfactory.

Fig 4 to 10 shows the isotherms at various temperatures from 380 to 600° C. At lower temperatures, starting from 380 to 550° C, the calculated liquidus isotherm matches very well with those of Gratton and Wooley (32). At higher temperatures the calculated curve deviates slightly from data of Gratton and Wooley (32), but agreement with

pseudobinary liquidus data of Wooley and Smith (17) is satisfactory.

Fig. 11 shows a comparison between the calculated values of Ansara et al (30), Blom and Plaskett (28)(regular solution model), and this study.

Calculated curve of this study satisfactorily matches the experimental data at all points. At the Ga rich side, the calculated curves of Ansara et al(30) and Blom and Plaskett(28) matches very well, but a lot of deviation comes in as it moves away.

4.3 GaSb-InSb system:

Fig 12 gives the calculated pseudobinary GaSb-InSb phase diagram together with the data points of Wooley and Smith (17), Wooley and Lees(18) and Blom and Plaskett (28) for comparison. The fit is very good for the liquidus but some deviation is seen for the solidus curve. The reason may be due to the fact that mutual diffusion coefficients of InSb and GaSb are very low. For compressed powdered samples, Wooley and Smith(17) and Wooley and Lees(18) reports more than eight weeks of annealing time was needed to get the sample sufficiently close to equilibrium. The possible reason for the little mismatch between the calculated solidus and experimental is that, the experimental points may not represent equilibrium composition.

CHAPTER 5

CONCLUSION

The binary Ga-In and the ternary Ga-In-Sb phase diagrams are calculated in this study. A quasi-sub-sub regular model is used to describe the thermodynamic properties of the liquid phase in the Ga-In and Ga-In-Sb systems. The solid phase in the Ga-In system is represented by Wagner's dilute solution model. The solid phase in the Ga-In-Sb system is represented by a regular solution model. Marquardt's Bsolve algorithm is used to optimize the values of model parameters. The fit to thermodynamic and phase diagram data using the optimized model parameters is found satisfactory.

Table 1: Comparison between the calculated (present study) and experimental phase diagram data of Ga-In system.

Reference	Eutectic temp.	Eutectic comp	Max.solubility of Ga in In.
	°C	at% In	at% Ga
French et et al (5)	16.0	16.0	14.8
Svirbely et al (6)	15.7	13.0	18.0
Heubner et et al. (8)	----	----	3.3
Predel et et al (10)	15.9	12.5	---
Hayes et al. (11)	15.8	14.2	----
Rao et al (12)	16.0	----	16.0
This study	15.7	14.0	5.0

Table 2: Values of model parameters for liquid phase for In-Sb, Ga-Sb and Ga-In binary systems

Parameter	In-Sb[*]	Ga-Sb[*]	Ga-In
A_1	-3469.1	-2221.6	533.440[**]
A_2	15.4310	15.3011	0.131575[$]
A_3	-1.9620	-2.0160	0.0
B_1	-1946.60	-1657.6	533.440[**]
B_2	9.1611	9.6150	0.131575[$]
B_3	-1.1960	-1.2631	0.0
C_1	300.27	213.90	0.0
C_2	0.3230	0.0435	0.0

$$\Delta_{fus}G^\circ(In) = {}^\circ G_{In}^L - {}^\circ G_{In}^s = 3263.52 - 7.5934 \ T \qquad J.mole.[*]$$

$$\Delta_{fus}G^\circ(Ga) = {}^\circ G_{Ga}^L - {}^\circ G_{Ga}^s = 5589.82 - 18.4529 \ T \qquad J.mole.[*]$$

$$\Delta_{fus}G^\circ(Sb) = {}^\circ G_{Sb}^L - {}^\circ G_{Sb}^s = 19874.0 - 21.9868 \ T \qquad J.mole.[*]$$

$$\Delta_{fus}G^\circ(InSb) = {}^\circ G_{InSb}^s - G_{In}^s - G_{Sb}^s$$
$$- 30252.3 - 0.246 \ T + 2.4284 \ T \ ln \ T. \qquad J/mole.[*]$$

$$\Delta_{fus}G^\circ(GaSb) = {}^\circ G_{GaSb}^s - G_{Ga}^s - G_{Sb}^s$$
$$- 41240.5 - 1.3941 \ T + 1.8426 \ T \ ln \ T. \qquad J/mole.[*]$$

[*] Sharma et al (5).
[**] Bros et al   (9).
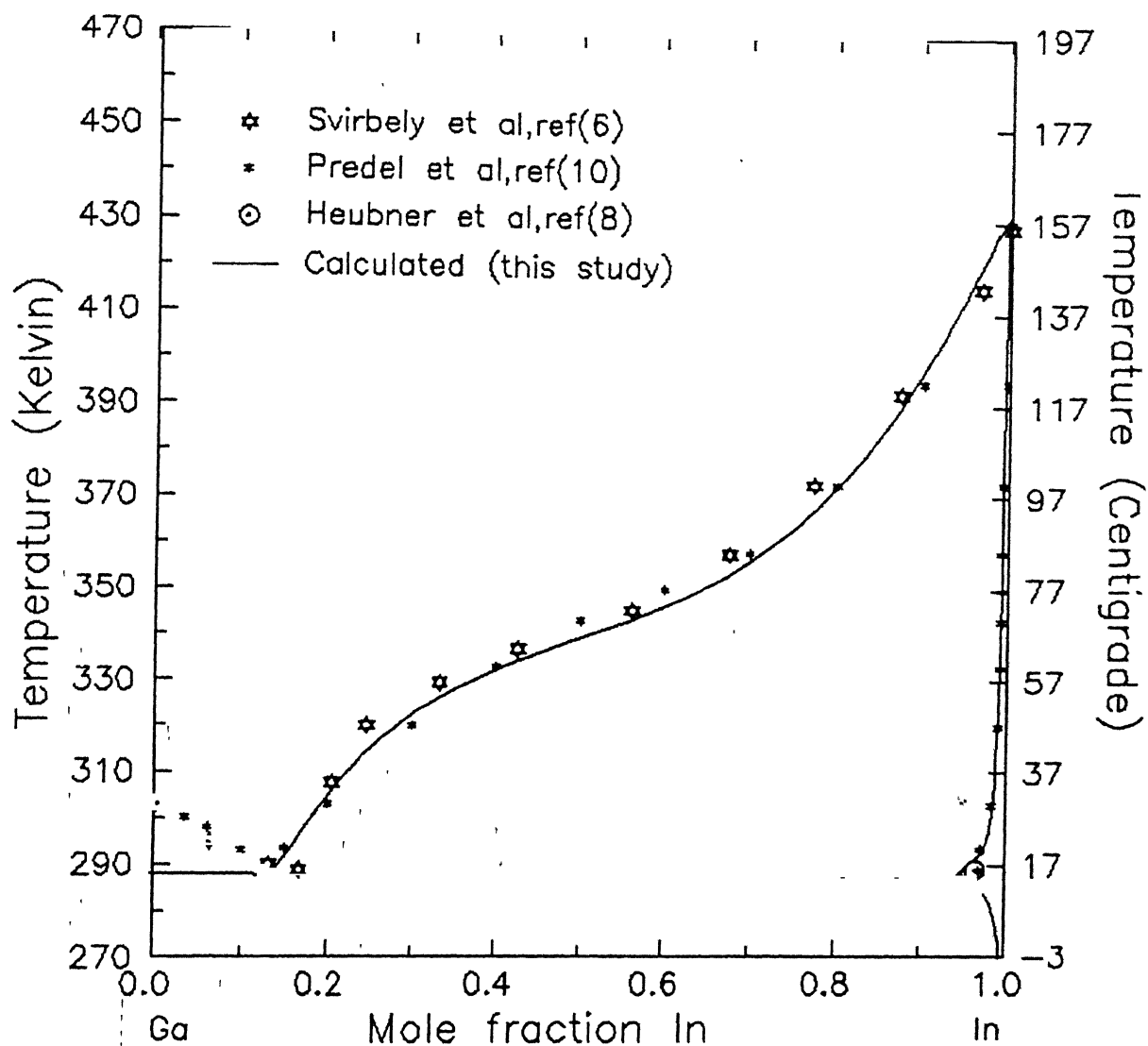[$] Calculated (this study).
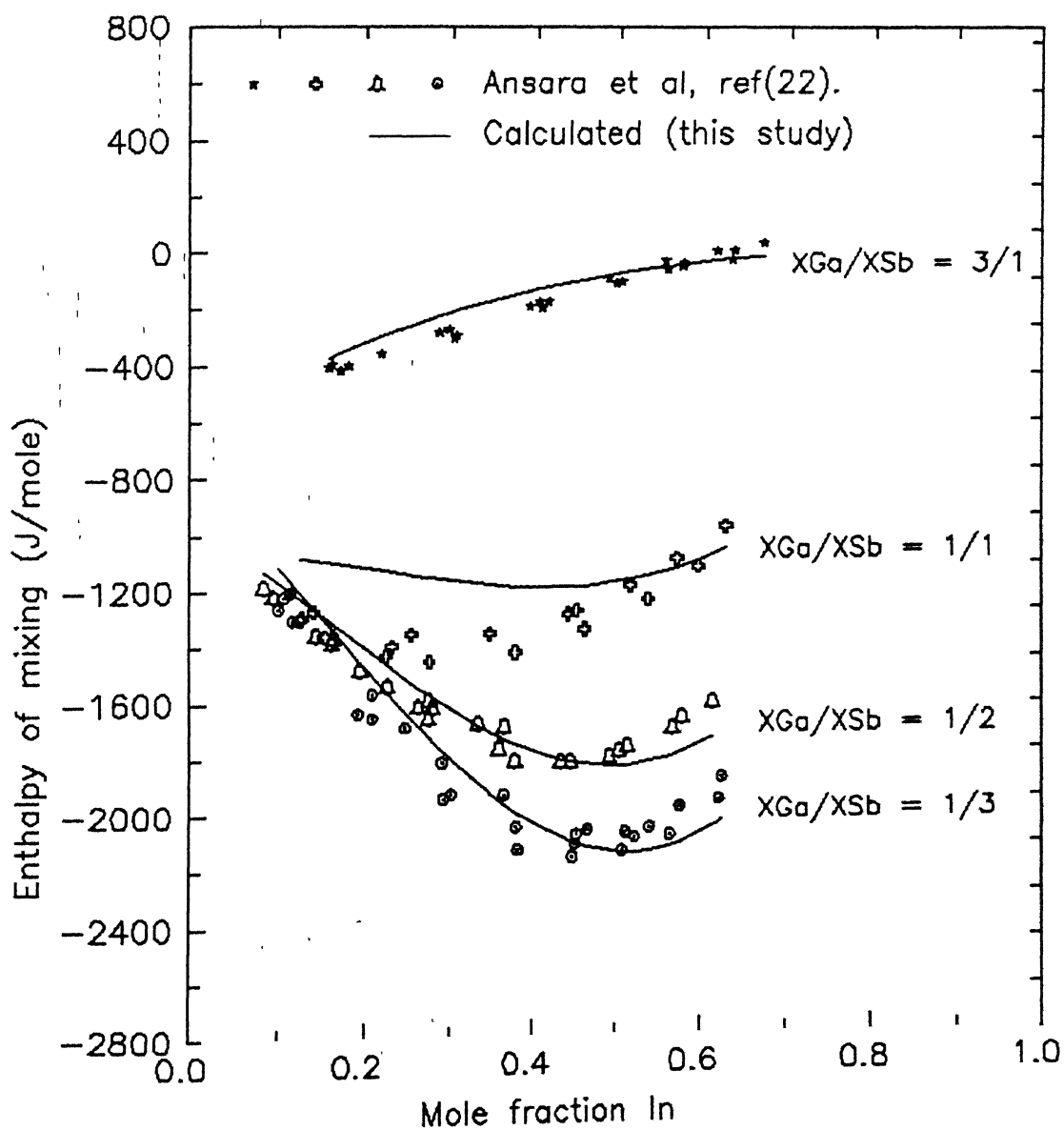
Fig2: Phase Diagram of Ga—In system.

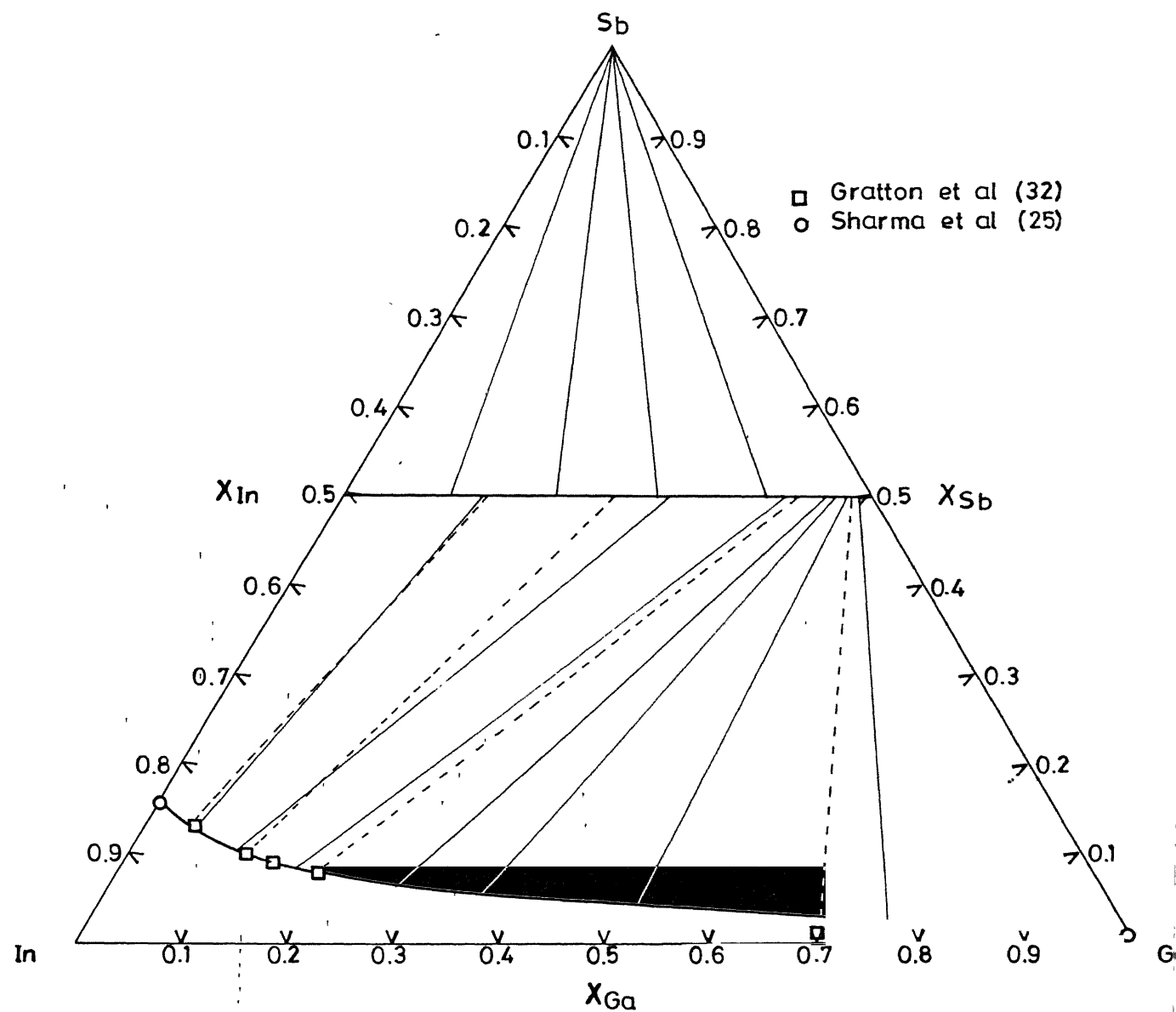Fig3: Enthalpy of mixing for Ga—In—Sb system at 1022 K.

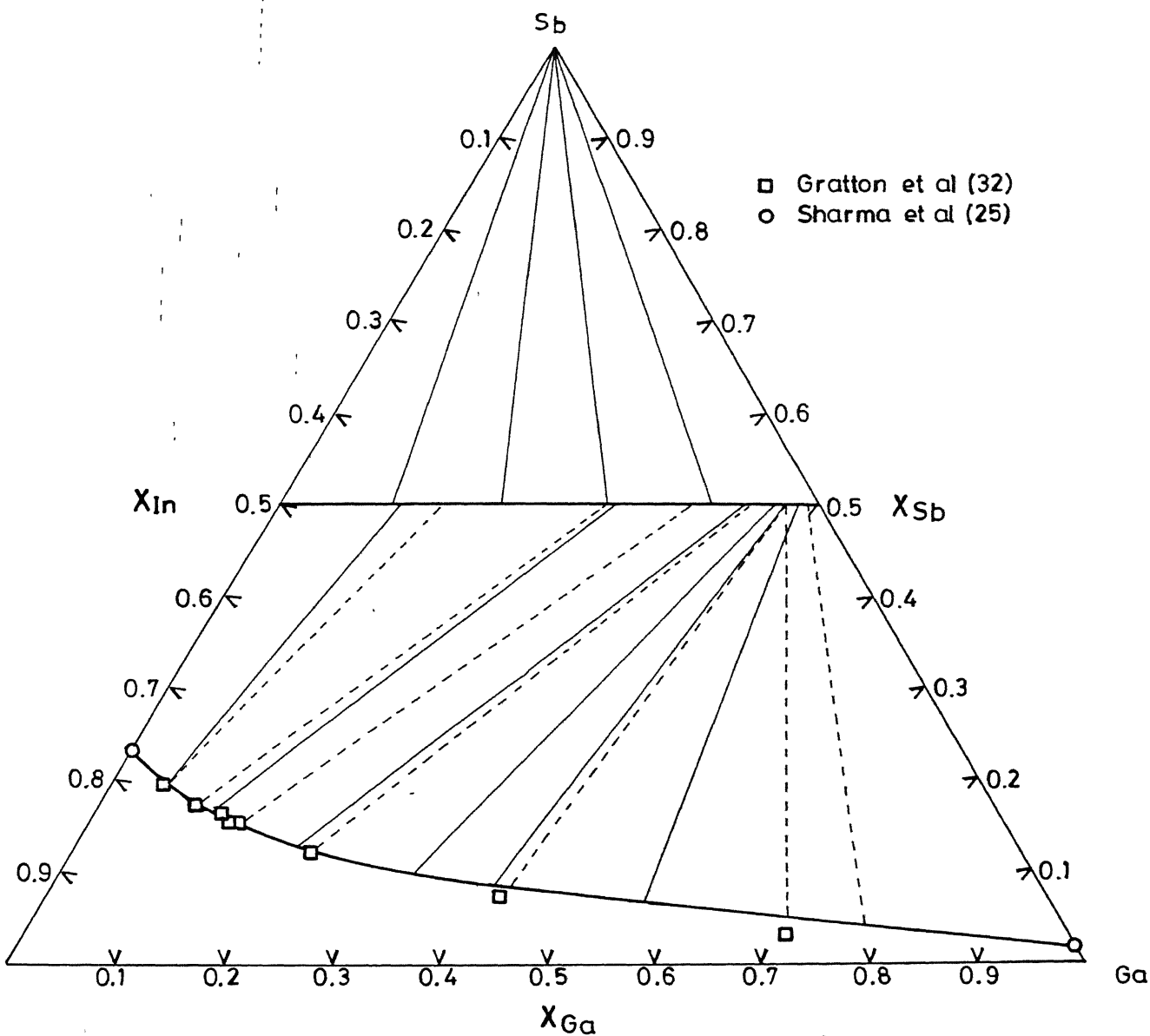Fig. 4.4 Liquidus Isotherm of Ga – In – Sb System at 380 °C .

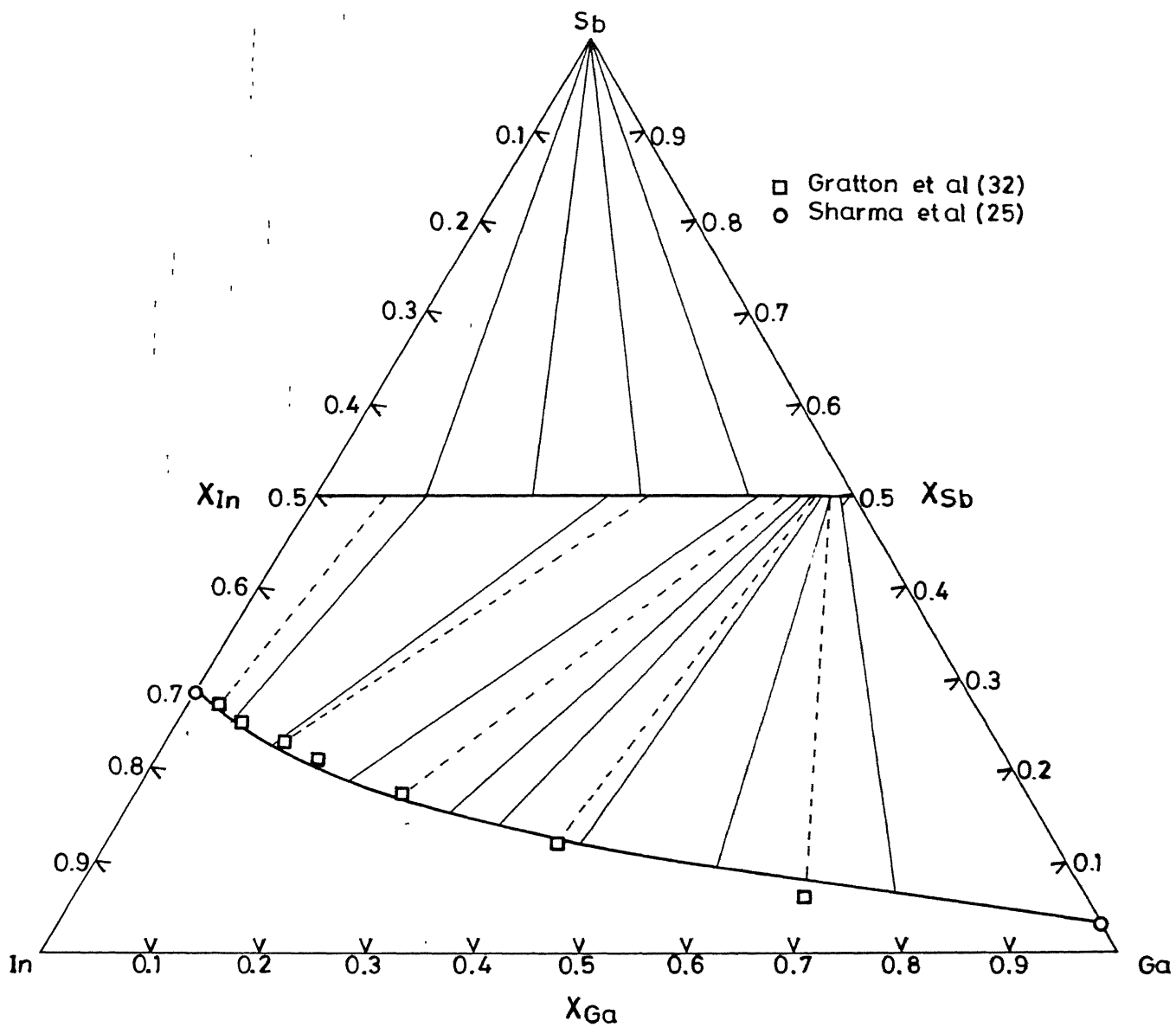Fig. 5   Liquidus Isotherm of Ga-In-Sb at 430 °C.

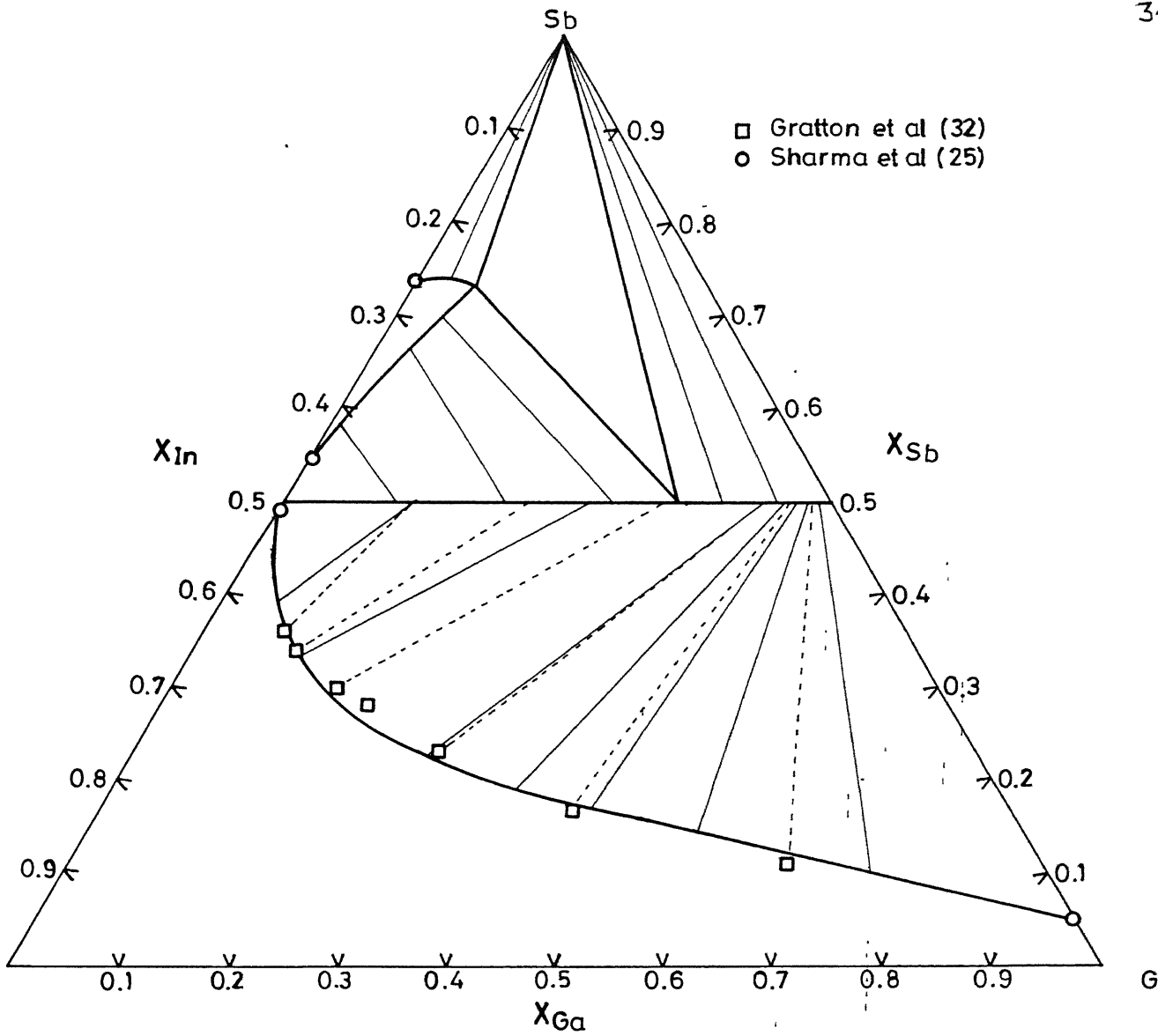Fig. 6   Liquidus Isotherm of Ga - In - Sb System at 475 °C.

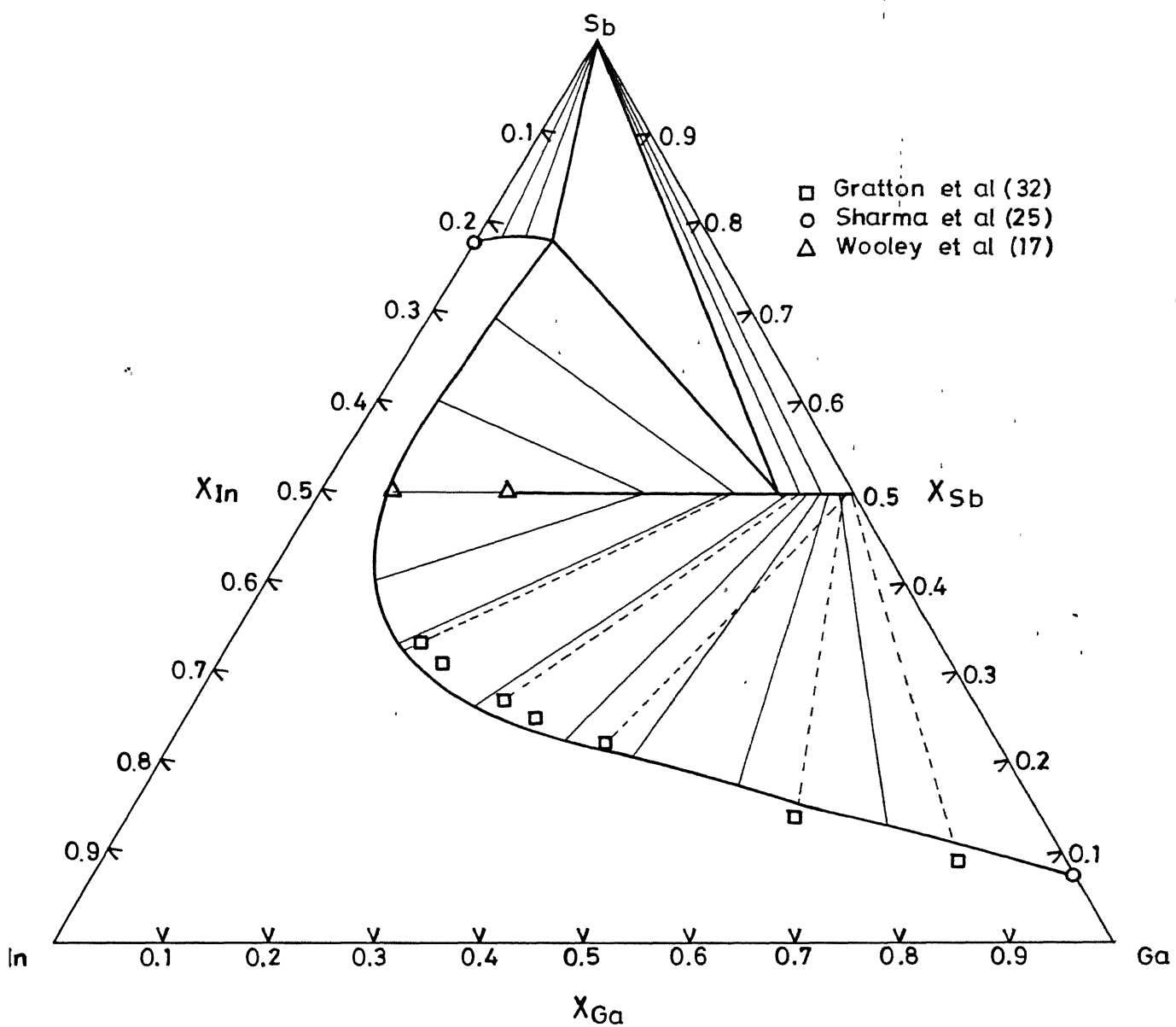Fig. 7   Liquidus Isotherm of Ga-In-Sb System at 525 °C.
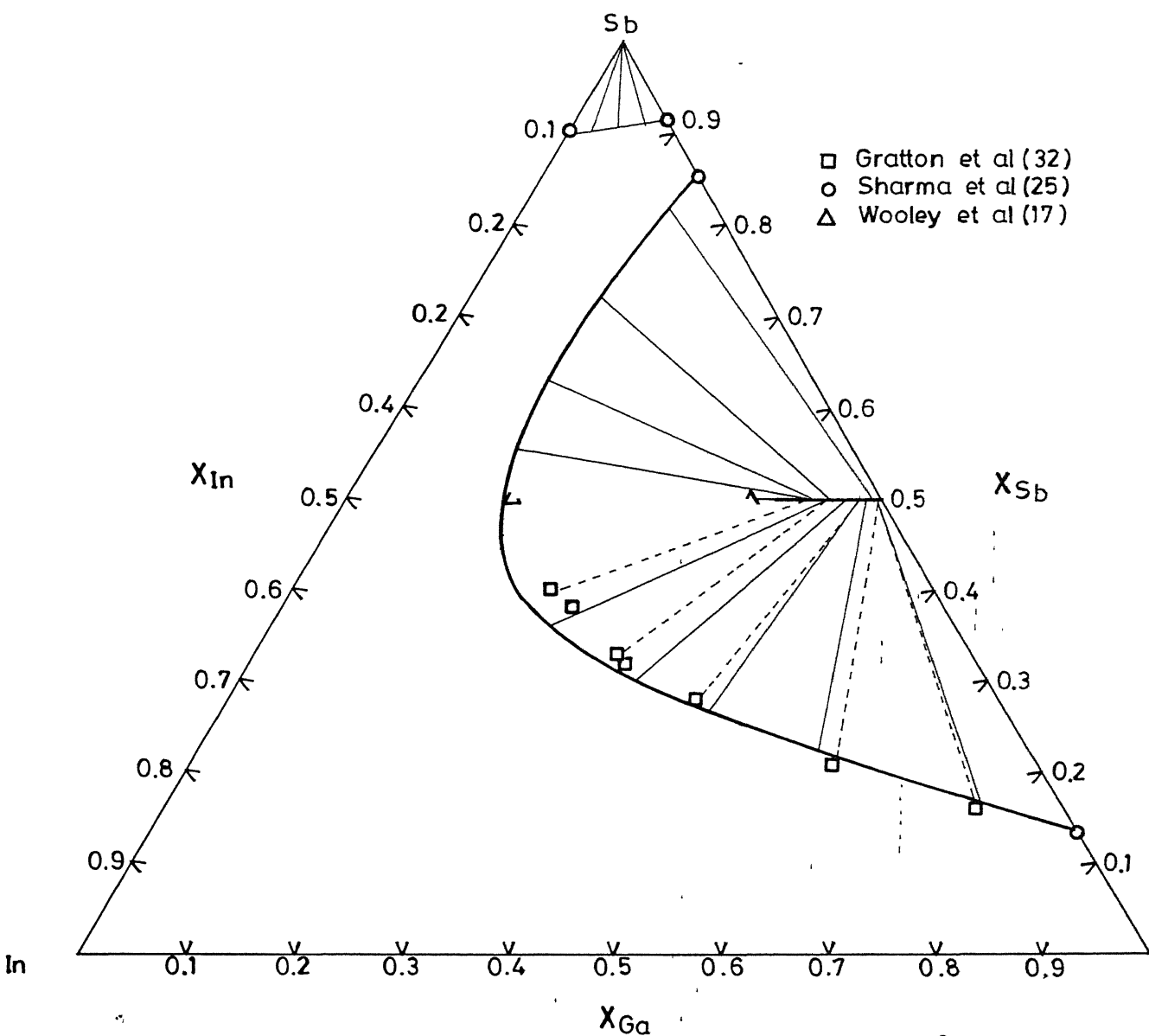
Fig. 8   Liquidus Isotherm of Ga-In-Sb System at 550 °C.
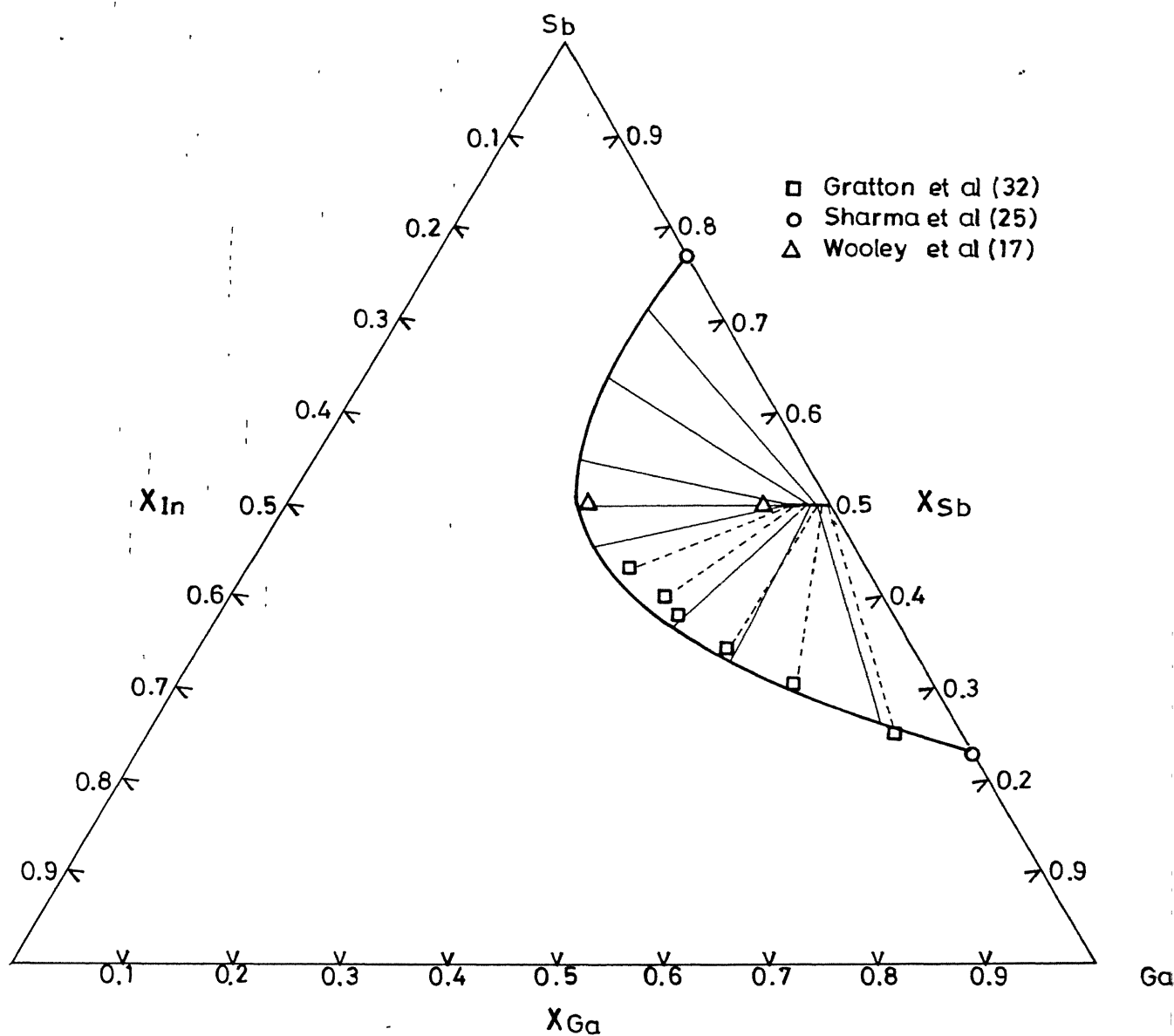
Fig. 9   Liquidus Isotherm of Ga-In-Sb System at 600 °C .

Fig. 10   Liquidus Isotherm of Ga – In – Sb System at 650 °C.
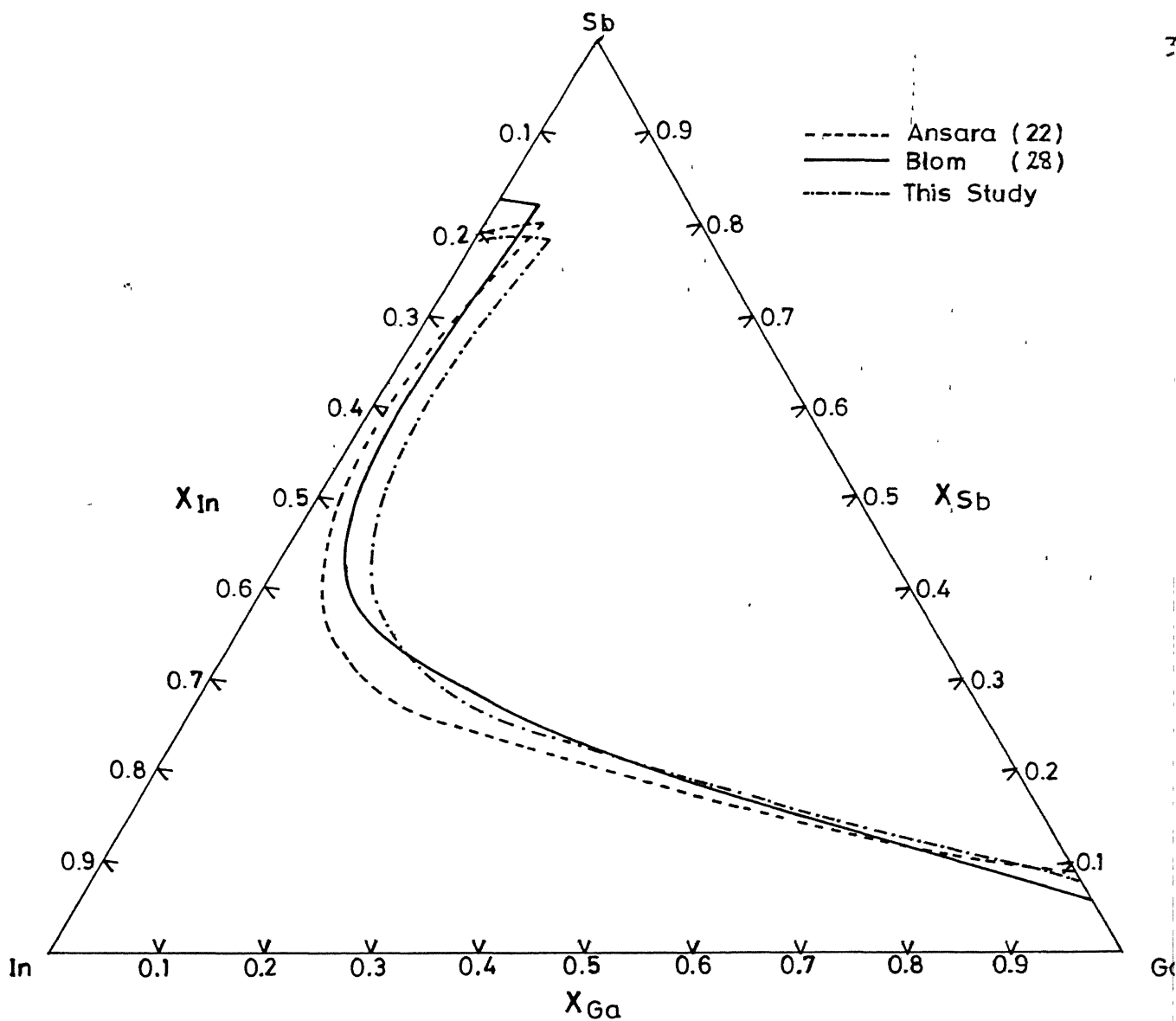
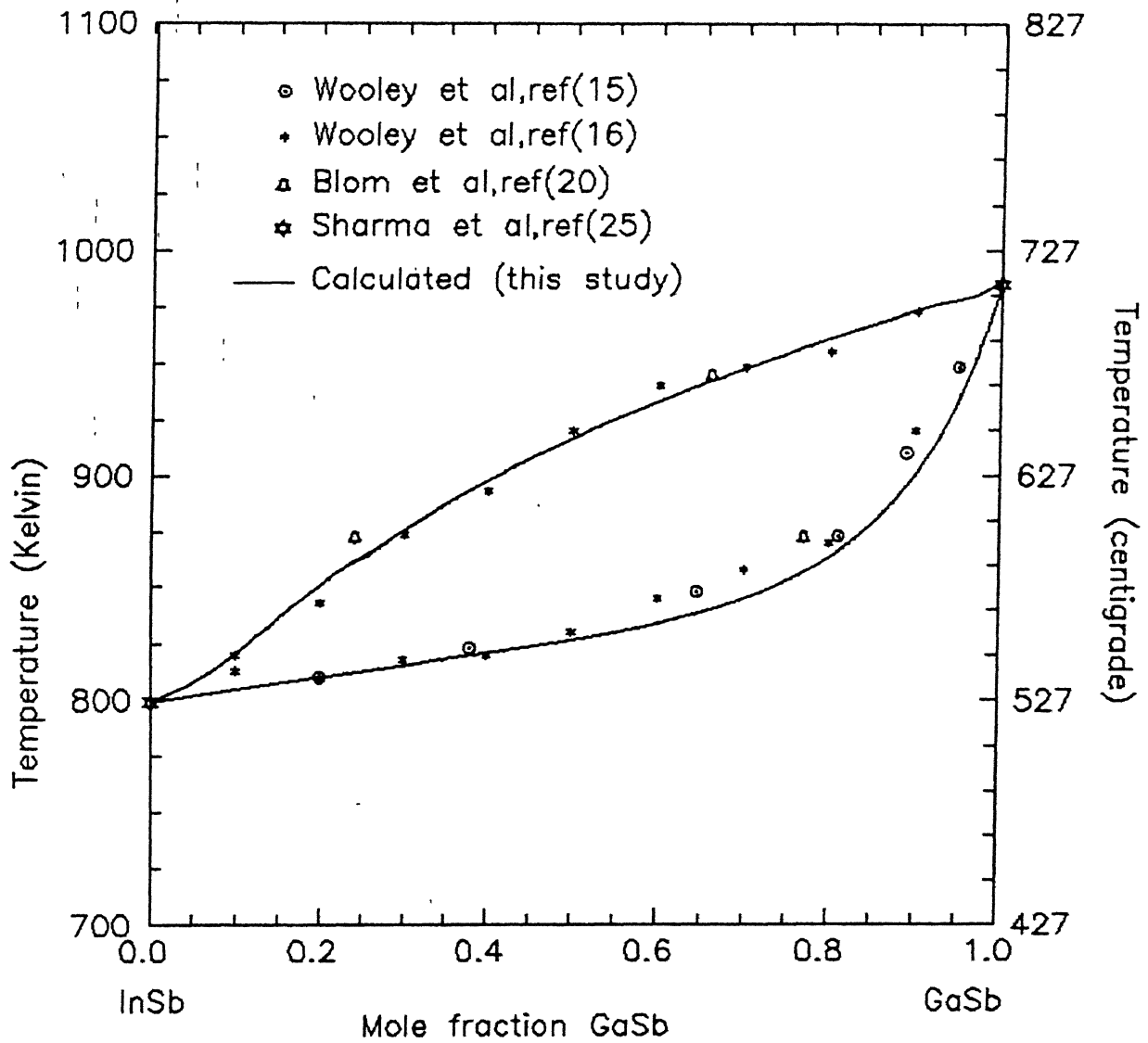Fig. 11. Comparison Between Liquidus Curves of Ga-In-Sb System at 550°C Calculated by Different Authors.

Fig12: Phase diagram for GaSb–InSb system

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